HC-Biiodegradation monitoring by geo-electrical measurements and CO2 analyses : field implementation

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HC-BIODEGRADATION MONITORING BY GEO-ELECTRICAL MEASUREMENTS AND CO_2 ANALYSES: FIELD IMPLEMENTATION

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ABSTRACT

Hydrocarbon contaminated aquifers can be successfully treated through biodegradation. However, *in situ* monitoring of the treatment is expensive, invasive and can be insufficient as the information provided is restricted to vertical profiles at discrete locations. An alternative method was tested in order to improve the robustness of the monitoring. Geophysical methods, Electrical Resistivity (ER) and Induced Polarization (IP), was combined with gas analyses, CO_2 concentration and its carbon isotopic ratio, to propose a non-destructive method for monitoring *in situ* biodegradation of hydrocarbons. It was tested at a BTEX-polluted site under aerobic bio-treatment. Geophysical monitoring show a more conductive and chargeable area which corresponds to the contaminated zone. Moreover, in this area, CO_2 emissions have been measured with an isotopic signature typical of biodegradation. Combining geophysics with gas analyses is thus promising to provide a new methodology for *in situ* monitoring.

KEYWORDS: biodegradation; hydrocarbons; monitoring; induced polarization; carbon isotopic fractionation

1. INTRODUCTION

Hydrocarbon contaminated aquifers can be successfully treated through biodegradation. However, this process still remains partially unexploited, mainly because *in situ* monitoring before and during soil treatment operations is often expensive and technically challenging. Indeed, where significant subsurface heterogeneity exists, conventional intrusive groundwater sampling campaigns can be insufficient to obtain relevant information as they are restricted to costly monitoring wells at discrete locations. New monitoring tools are needed to overcome these limitations and make the *in situ* bioremediation more reliable, robust, as well as economically competitive.

Geo-electrical techniques, especially induced polarization (IP), can be used to study the effects of biodegradation (Atekwana and Atekwana, 2010). Indeed, biodegradation processes modify ground electrical properties because they alter biogeochemical conditions: bacteria modify local redox conditions; microbial activity can produce organic acids that affect the pore water conductivity; during microbial growth and formation of biofilms, biomass can clog pores and potentially change the porosity and hydraulic conductivity. Thus, IP is expected to be an effective non-intrusive tool to monitor bioremediation.

Geo-electrical methods are often used in conjunction with geochemical measurements (temperature, pH, redox potential, water conductivity and dissolved oxygen content) to detect changes in the chemical properties of the soil and groundwater caused by microbial metabolism. In the aim to propose a complete non-destructive monitoring methodology, we follow microbial metabolism by studying gas emissions at the ground surface. Indeed, biodegradation of organic compounds induces CO_2 production and isotopic fractionation of carbon. CO_2 produced by hydrocarbon degradation may be distinguished from that produced by other processes based on the carbon isotopic compositions characteristic of the source material and/or fractionation accompanying microbial metabolism. Indeed, carbon isotopic signature of CO_2 reaches that of contaminant and it can be accompanied by significant carbon isotope fractionation. (Aggarwal and Hinchee, 1991).

From these findings, we propose to combine geo-electrical methods and gas analyses to develop a new non-invasive technique for monitoring *in situ* biodegradation of hydrocarbons. These tools were previously tested at laboratory scale in sand-columns with toluene as model pollutant and an exogenous bacterial strain. The promising results from the column study allowed implementing a monitoring strategy at the field scale. The site is a gasoline station where gasoline and diesel fuels leaked fifteen years ago. The fraction of benzene, toluene, ethyl-Benzene and xylenes (BTEX) represent a consequent part of the pollutants. A trench supplies the necessary oxygen to the aquifer in order to stimulate the aerobic bacterial processes. ER and IP surveys and CO_2 analyses have been performed since February 2014.

2. MATERIALS AND METHODS

2.1 Site

The field site studied is a gasoline station where gasoline and diesel fuels leaked in 1997 (Figure 1.A). It is still in activity but the former tank installation (source of contamination) was dismantled. Several boreholes had been drilled for previous studies on this site. These studies showed that: the ground is mainly composed with silts and clays and it has a low permeability (between 10^{-6} and 10^{-7} m/s); the direction of flow is North-West; the water table is between 2.5 and 4.5 m depth; there is a presence of hydrocarbons (BTEX) in the area of the former tank installation; there are indications of a natural attenuation which prove the presence of a bacterial flora, such as absence of dissolved oxygen, that match the BTEX plume in water.

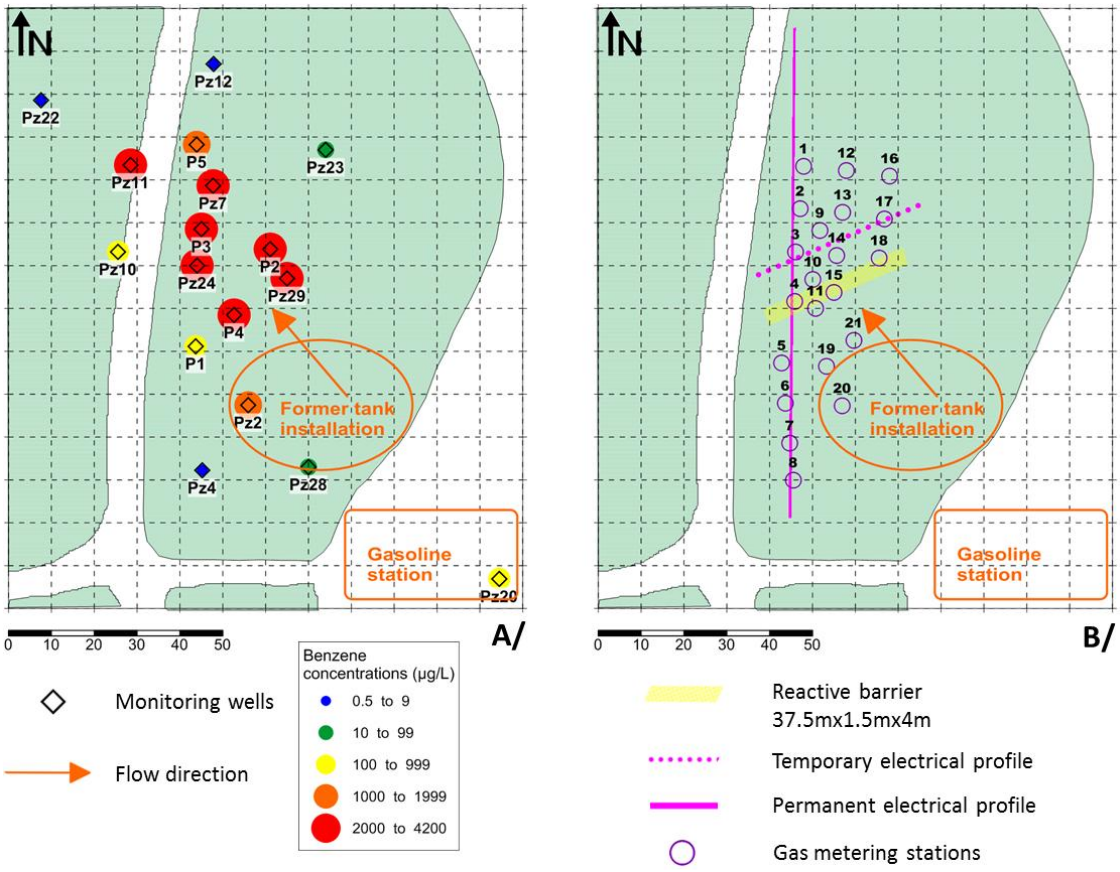

Figure 1. A/ Map of the site showing gasoline station, former tank installation, monitoring wells and the benzene concentrations measured in water. B/ Map of the site showing the reactive barrier and the monitoring disposal: electrical profiles and gas metering stations.

As a natural biodegradation of hydrocarbons is already in process, a bio-treatment by an oxygen supply to stimulate aerobic metabolic processes has been decided for this site. A permeable reactive barrier was implemented to stop the plume migration. Diluted H_2O_2 is added to pumped water in the barrier and reinjected below water table.

2.2 Electrical measurements

Electrical resistivity (ER) and Induced polarization (IP) measurements are made by injecting an electrical current into the ground between two current electrodes and making measurements of the induced voltages between two receiving electrodes. By comparing the transmitted signal to the received signal we can analyze the electrical response of the ground. In ER measurements, we obtain resistivity (the ability of the ground to conduct electrical current) by multiplying the resistance (I/V) by a geometrical factor (which depends of disposal geometry). In time domain IP measurements, we measure the relaxation time of the potential when the current is switched off. It allows calculating the chargeability, the capacitive properties of the ground.

Time domain IP and ER surveys were performed regularly since February 2014 to monitor the stimulated biodegradation and the progress of depollution until soil cleanup. There is a permanent (buried) electrical profile perpendicular to the reactive barrier, 120m long (60 electrodes separated by 2m) and temporary profile parallel to the barrier (48 electrodes separated by 1m) (Figure 1.B). Both profiles are transverse to the contaminant plume. Measurements are taken every two days for the permanent profile, and every two months for the temporary one.

2.3 CO_2 analyses: emissions fluxes and carbon isotopic ratio

CO_2 concentration and $\delta^{13}C$ isotopic ratio in produced CO_2 are measured by infrared laser spectroscopy. The $\delta^{13}C$ is the difference between the isotopic ratio $R = {}^{13}CO_2/{}^{12}CO_2$ of the sample and of a standard. ($\delta^{13}C(‰) = [({}^{13}C/{}^{12}C)_{ech}/({}^{13}C/{}^{12}C)_{VPDB} -1]*1000$, with $({}^{13}C/{}^{12}C)_{VPDB} = 0.011237$). The spectrometer is directly connected with a closed accumulation chamber set on a permanent PVC cylinder collar (diameter = 30cm) sunk into the soil to measure CO_2 emission fluxes and $\delta^{13}(CO_2)$. We have 21 measuring points on the site, upstream, above and domnstream the reactive barrier (Figure 1.B). Measurements are performed every two months since February 2014.

3. RESULTS AND DISCUSSION

3.1 Electrical measurements

Time Domain IP and ER data of the permanent profile are represented on resistivity and normalized chargeability (ratio of raw chargeability over resistivity) sections (Figure 2). On the resistivity section, we show a conductive zone at 2-6m depth, between 50 and 72m . This area is also very chargeable and it may match the top of the water table, where hydrocarbon biodegradation produced conductive and chargeable metabolites. Moreover, we can clearly see that the more conductive and chargeable zone matches the polluted zone defined by geochemical borehole analyses (Pz24, P7), downstream the former tank installation.

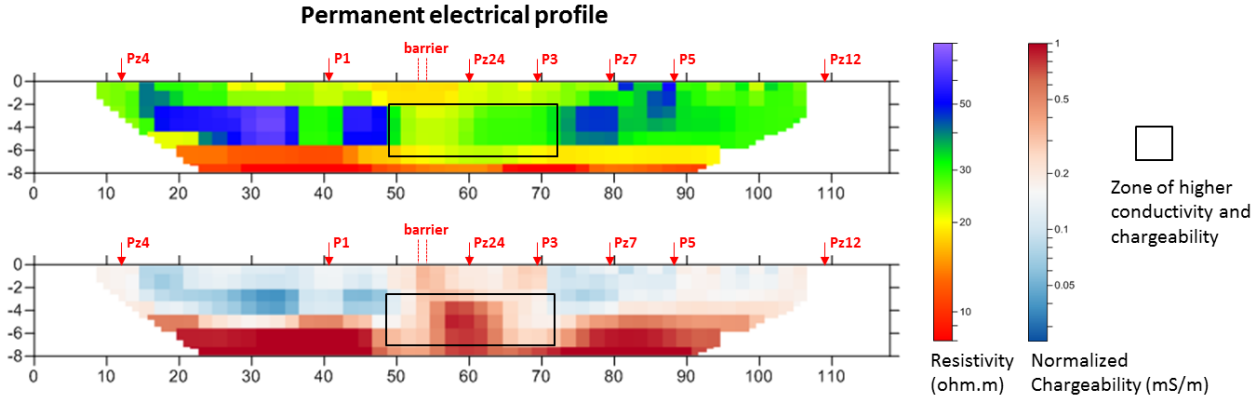

Figure 2. Resistivity and normalized chargeability sections across the plume for the permanent electrical profile, May 2014.

3.2 CO_2 analyses

The same zone produces high CO_2 fluxes (up to 1500 ppb.s^{-1}, three to four times higher than a non polluted soil) (Figure 3). It is probably due to bacterial respiration. Moreover, in this area, CO_2 emissions have been measured with an isotopic signature typical of hydrocarbon biodegradation. Indeed, $\delta^{13}(CO_2)$ are measured between -27 and -30‰ since February 2014, in accordance with the BTEX signature measured in water (around -25 – -26‰). Moreover, results show a light isotopic fractionation (1 to 3‰) where $\delta^{13}(CO_2)$ is lower than δ^{13}(hydrocarbons source), which means that molecules with light isotopes (^{12}C) are prefered by bacterial metabolism.

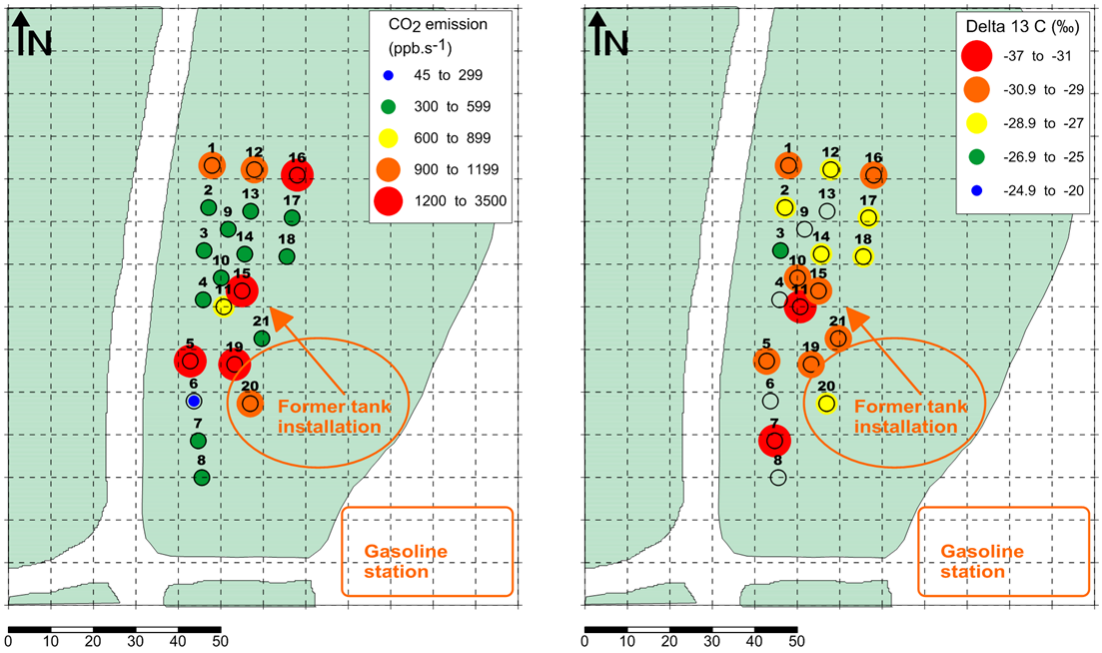

Figure 3. Maps of measured CO_2 emissions (left) and its carbon isotopic ratio (right), July 2014.

4. CONCLUSIONS

Results have shown a more conductive and chargeable zone at around 3 meters depth, which matches the polluted zone defined by geochemical borehole analyses. Moreover, CO_2 emissions have an isotopic signature typical of hydrocarbon biodegradation. Our results argue for combining geophysics with gas content and isotopic measurements to monitor zones of biodegradation and will allow us to give a practical non-intrisive method of monitoring and evaluating *in situ* remediation.

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REFERENCES

P. K. Aggarwal and R. E. Hinchee, 1991. "Monitoring in situ biodegradation of hydrocarbons by using stable carbon isotope." Environmental Science & Technology **25**: 1178-1180.

E. A. Atekwana and E. A. Atekwana, 2010. "Geophysical signatures of microbial activity at hydrocarbon contaminated sites: a review." Surveys in Geophysics **31**: 247-283.

M. Auffret, D. Labbé, G. Thouand, C. W. Greer and F. Fayolle-Guichard, 2009. "Degradation of a mixture of hydrocarbons, gasoline and diesel oil additives by Rhodococcus aetherivorans and Rhodococcus wratislaviensis". Applied and Environmental Microbiology, **75**: 24, 7774-7782.